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Final Report:
High-Altitude NO and NOy Measurements Using a New, Lightweight Chemiluminescence Instrument (NCC2-786)

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Abstract of Research Objectives

Field measurements of NO and NOy were proposed, using a new lightweight dual-channel NO/NOy instrument to investigate processes regulating NOx, NOy and ozone in the lower and middle stratosphere. The measurements were intended to be part of the HSRP 1994 field program and to complement ER-2 measurements planned for the Airborne Southern Hemisphere Ozone Experiment (ASHOE). Altitudes above the operational envelope of the ER-2 were targeted, in the tropics and middle latitudes. A fully operational 35 kg instrument was planned, to be tested in the stratosphere and incorporated into a lightweight payload with ClO, BrO, ozone, T and P and a tracer instrument (probably a tunable diode laser spectrometer then under development) on the Perseus A.

Summary of Results

Instrument development

The instrument was designed to measure NO using chemiluminescence and NOy by catalytic conversion to NO followed by chemiluminescence. The design achieved light weight and low power using measurements at ambient pressure, instead of the low-pressure design currently in use. In order to obtain the large sample mass flows needed for high sensitivity at ambient pressure, an ultra-light Roots-type pump was designed and implemented.

Components and sub-assemblies were fully procured and extensively tested. Perseus A did not emerge, nor did any other RPA platform. Instrument integration did not take place, because the lack of a platform precluded development of the crucial interface between the hot gold catalyst and the platform.

Although the instrument development could not be completed without a platform, the work resulted in significant advances in our understanding of the NOy catalytic measurement technique and in the resolution of long-standing issues regarding reaction efficiency and null artifacts in the chemiluminescence technique. Since these are the primary methods in use for atmospheric measurements of NOx and NOy, this work provided science value to the program.

Studies defining characteristics of the NOx and NOy measurement techniques in wide use for atmospheric observations.

We performed extensive laboratory studies aimed at optimizing the detection methods and undertook detailed investigations to characterize the NOy catalytic conversion process over a broad range of conditions, including those relevant to the current controversy surrounding tropospheric NOy measurements. We also made significant progress in developing alternative detection schemes.

1. NO Chemiluminescence Detection

We fabricated and tested several new designs for the chemiluminescence cell. The final design has a higher sensitivity, lower zero artifact (in the lab), and lower total instrument weight (by a factor of 5) than previous implementations. Kinetic modeling of the chemiluminescence cell was undertaken, allowing optimization of the detector performance within the power and gas-consumption constraints applicable to a range of operational scenarios.

2. NOy Catalytic Conversion

Using the NOy species NO, NO_2, HNO_3, and isopropyl nitrate and the potential interferences HCN, CH_3CN, NH_3, and N_2O we determined (a) artifacts and (b) conversion efficiencies as a function of reducing-agent concentration with both H_2 and CO; (c) the effect of humidity and O_3 on conversion efficiency; (d) loss of NO in the catalyst and on other metallic and non-metallic surfaces; and (e) the efficacy and suitability as catalytic converters (or inlets) of 24 k gold, 18 k gold, gold doped with 1% cobalt, silver, platinum, stainless steel, and quartz.

The most surprising results were the discovery of a gas-phase process that contributes to the conversion of HNO_3 to NO and the identification of conditions that produce oxidizing sites on/in the catalyst, allowing HCN, CH_3CN, and NH_3 to be converted to NO with high efficiency.

A manuscript has been accepted for publication that provides a detailed description of these measurements and discusses their implications for in situ measurement of atmospheric NOy (including recommendations for performing measurements using catalytic conversion).

New Directions

Laser-induced fluorescence (LIF) is a highly sensitive and specific spectroscopic technique for detection of a number of small molecules, including NO. The size, weight, complexity, and power requirements of existing laser systems used to generate the required UV radiation have prevented LIF from being widely applied to field measurements. In collaboration with Lew Goldberg of the Naval Research Laboratory in Washington, DC, we investigated using semiconductor lasers to power a compact, lightweight, efficient (low power consumption, low heat generation), solid-state, inexpensive sources of tunable, narrow-bandwidth UV radiation to be used for LIF. We frequency- quadrupled the output of a high-power diode laser to generate tunable light near 215 nm, the wavelength required for NO LIF. These pilot studies have been published and led to the submission of a patent application. We received a grant from the NSF to continue this research.

Journal Publications

1. D.A.V. Kliner, B.C. Daube, J.D. Burley, and S.C. Wofsy, Laboratory Investigation of the Catalytic Reduction Technique for Measurement of Atmospheric NOy, J. Geophys. Res. (accepted, 1997).

2. L. Goldberg and D.A.V. Kliner, Deep-UV Generation by Frequency Quadrupling of a High-Power GaAlAs Semiconductor Laser, Opt. Lett. 20, 1145 (1995).